

Intralines of Quasi-Conical Intersections on Torsion Planes: Methylamine as a Case Study

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Recently we reported on a novel feature associated with the intersection of the two lowest states $^1A'$ and $^1A''$ of the methylamine (*J. Chem. Phys.* **2008**, *128*, 244302). We established the existence of a finite (closed) line of conical intersections (*ci*), namely, a finite seam, located in the HC–NHH symmetry plane, a line that is formed by moving a single hydrogen on that plane while locking the positions of the (six) other atoms. In the present article, this study is extended to the corresponding torsion planes formed by rotating the methyl group around the CN axis. The torsion planes, in contrast with the HC–NHH symmetry plane, do not satisfy the symmetry feature that enables the seam just mentioned. Nevertheless, the calculated nonadiabatic coupling terms (NACTs) resemble features similar to those encountered in the HC–NHH symmetry plane. Following a tedious numerical study supported by a theoretical model (Section III), it was verified that these NACTs may become similar to those on the symmetry plane, sometimes even to the level of almost no distinction, but lack one basic feature; namely, they are not singular and therefore do not form topological effects.

I. Introduction

The study of the electronic nonadiabatic coupling terms (NACTs) and Jahn–(Renner–)Teller intersections concentrated, for the last two decades, mainly on small molecules, namely, triatomic and tetra-atomic systems.^{1–15} Our approach, which is based on ab initio treatments,^{1,4–6} was recently extended to larger molecular systems, and among them we performed a detailed study of the methylamine molecule, CH_3NH_2 , consisting of seven atoms.^{16a,b} While saying that, we mention that there are other kind of studies associated with Jahn–Teller intersections for large molecular systems that are based on the so-called vibronic coupling approach¹⁷ (and therefore avoid the NACTs). The structure of the molecule is given in Figure 1, where it can be seen that the methyl group, CH_3 , is separated from the amine group, NH_2 , by the CN bond. This molecule has been an issue of interest for a long time because it comprises two strongly coupled large amplitude motions, specifically, the torsion of the methyl top and the inversion of the amine group.¹⁸ Several experimental studies provided evidence of the principal channel for photodissociation in the first absorption band corresponding to the N–H bond fission.^{19–23} Very recently,²² it was shown that in the vibrationally mediated photodissociation of CD_3NH_2 , about 90% of H and D observed products are hydrogen photofragments released from the amine group, and the remaining 10% are the deuterium released from the methyl group.

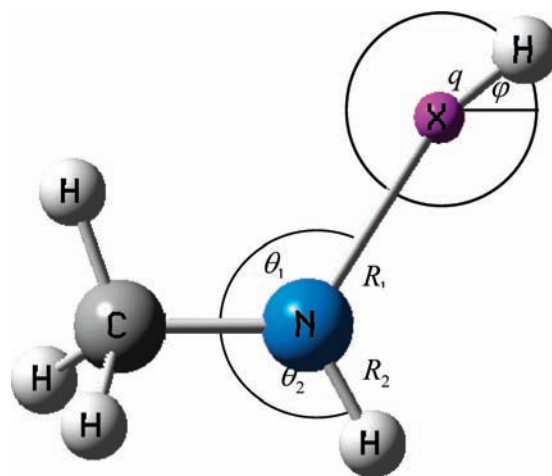


Figure 1. Equilibrium structure of methylamine. Symmetric HC–NH₂ plane. The coordinates θ_1 and R_1 show the position of the test hydrogen (with respect to the nitrogen). These coordinates are varied during the *ci* search. (The coordinates θ_2 and R_2 are held fixed during this process.) The polar coordinates q and φ show the position of the test hydrogen with respect to an assumed point close to a possible *ci* point.

Early numerical treatments revealed cuts through the ab initio potential energy surfaces for the ground, $^1A'$, and the first excited, $^1A''$, states of methylamine. In particular, it was pointed out that the $^1A''$ state potential that leads to the breakup of the N–H bond is characterized by a small barrier ($\sim 3000 \text{ cm}^{-1}$) at short range, which seems to be followed, at somewhat larger bond extensions, by a conical intersection (*ci*) formed by the above-mentioned states, both belonging to the C_s symmetry.²⁴ This study, just like ours,¹⁶ was carried out for the nuclear configuration where the five atoms HC–NHH form a plane that is a plane of symmetry; therefore, the above-mentioned two

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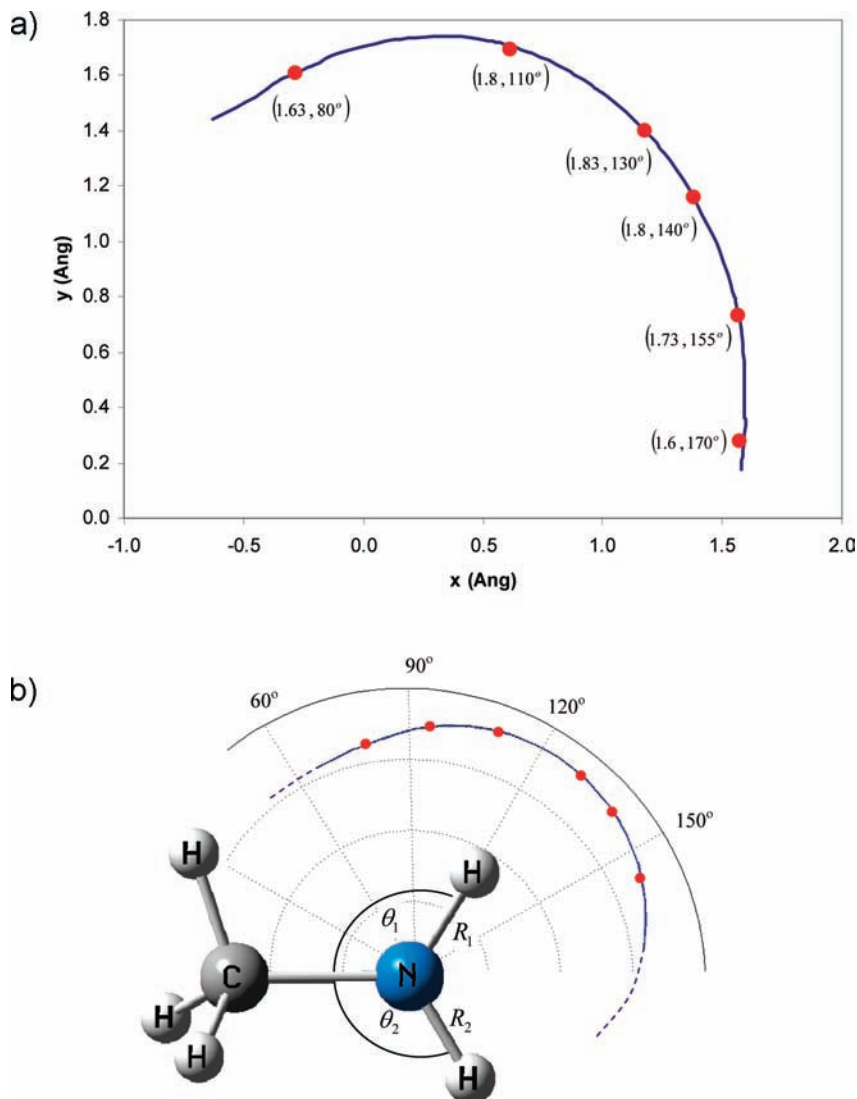


Figure 2. Intraseam located on the symmetry plane and the intra-quasi-seam located on the torsion plane $\vartheta = 30^\circ$. (The seam and the quasi-seam overlap to the extent that they cannot be distinguished.) The curves presented are for a system of coordinates situated at the nitrogen (and calculated for the case in which the second amine hydrogen is located at $R_2 = 1.0 \text{ \AA}$ and $\theta_2 = 120^\circ$; Figure 1). The points on the curves indicate the position of the centers of circular contours along which are calculated the NACTs (Figure 3) and the corresponding values of $\alpha(q|\vartheta)$ and $\tilde{\alpha}(q|\vartheta)$. (a) Corresponding x - y plane (where $x = R_1 \cos(\pi - \theta_1)$ and $y = R_1 \sin(\pi - \theta_1)$). (b) Plane including the other components of the molecule.

states, ${}^1A'$ and ${}^1A''$, are forced to have a different symmetry. (The implication of this fact is discussed below.)

Our study based on the MOLPRO package^{25,26} revealed one of the more interesting results, namely, that the two mentioned states are coupled not by a single *ci* (or several *ci*'s) but by a line of *ci*'s that is fully detected by moving the hydrogen in one single plane, in this case, the plane of symmetry (See Figure 2). Continuous lines of *ci*'s are known as seams, but this one is somewhat different. In all previous studies,^{1,4,6-8,10,15} the seams were located by moving atoms at a series of planes where in each plane is detected one (sometimes more than one) *ci* point(s). The seams detected in this way are lines in configuration space for which there is no reason to believe that they are located in a single plane. In the present case, the atom we chose, namely, an amine hydrogen, is constrained to move on the HC-NHH plane only; nevertheless, a continuous line of *cis* (a seam) fully located in that plane was revealed¹⁶ (See Figure 2a,b). In what follows, we term this (amine) hydrogen as a test particle (reminiscent of test particles to detect, e.g., electric fields).

This unusual situation is responsible for two additional phenomena: (a) Along any (open) contour in the above plane

formed by the test particle that intersects this seam, a narrow, spiky, NACT is formed (Figure 3) for which the area under it is $\sim \pi/2$.^{16a,16b} (b) It was shown, following a careful application of MOLPRO,²⁵ that the corresponding topological (Berry) phase is zero. In a more recent publication^{16b} is presented a model that analyzes these findings.

In general, the existence of such a seam cannot be justified. It is well known that for two states to form degeneracy at a given point, two conditions have to be fulfilled, namely²⁷

$$W_{11} - W_{22} = 0 \quad (\text{I})$$

$$W_{12}(=W_{21}) = 0 \quad (\text{II})$$

where W_{ij} ($i, j = 1, 2$) represents the matrix elements of the electronic Hamiltonian (also known as the diabatic potentials). For a randomly selected plane, these conditions are at most satisfied at isolated points. If, however, a study is carried out with respect to a plane of symmetry and the two states are of different symmetries (as indeed ${}^1A''$ and ${}^1A'$ are), then condition II is satisfied trivially

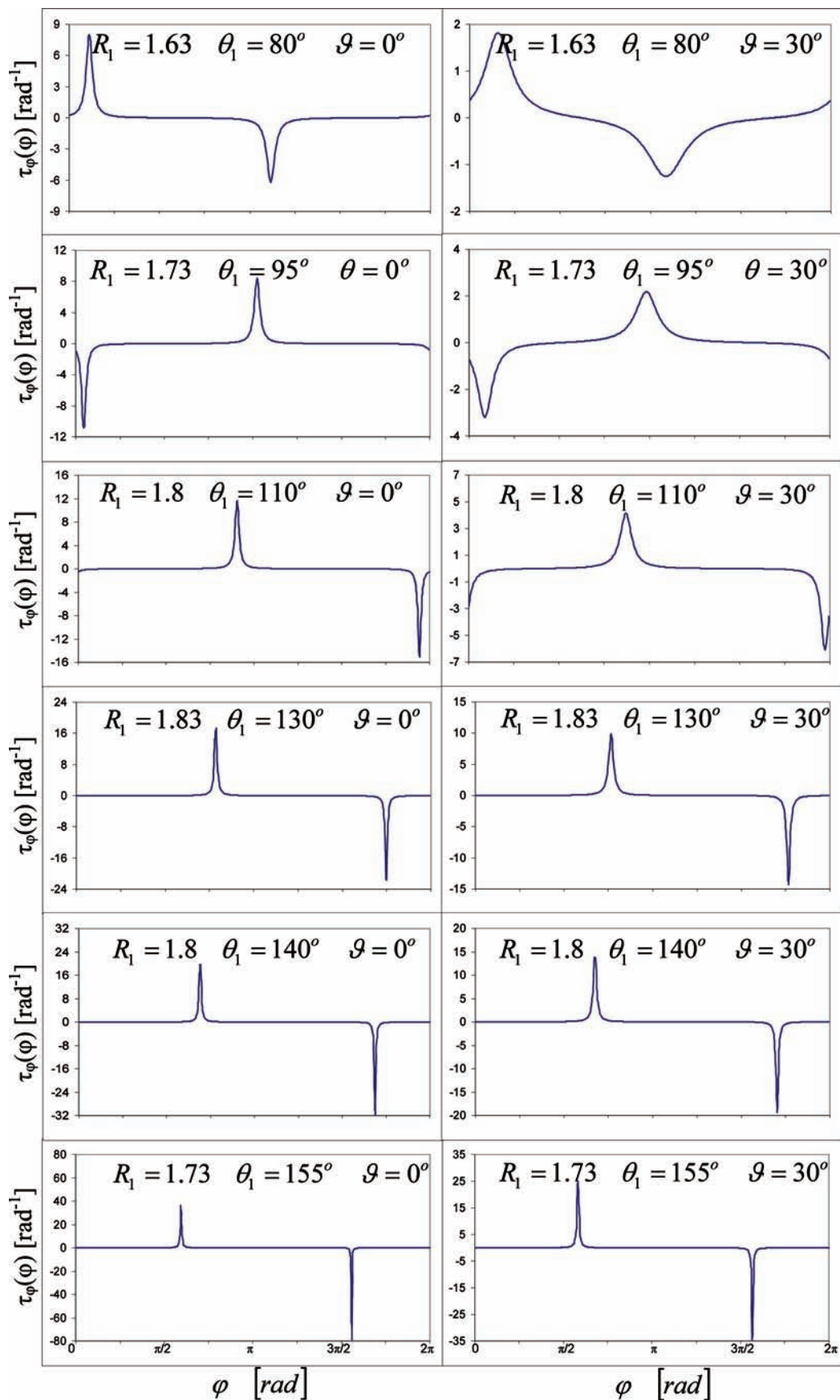


Figure 3. Angular NACTs (τ_ϕ) presented as a function of ϕ for $q = 0.1 \text{ \AA}$ calculated at six different locations along the seam (as calculated on the symmetry plane) and the quasi-seam (as calculated on the torsion plane). (See Figure 2.) The first column contains results related to the seam, and the second column contains results related to the quasi-seam.

by symmetry. As a result, we are left with only one requirement as given by eq I, which can be fulfilled along a line in a 2D space, namely, the above-mentioned plane. This phenomenon is extensively discussed in ref 16.

In the present article, the two-state study is extended to torsion planes, for which symmetry arguments are not valid anymore. These planes are formed by rotating the methyl group around the CN axis by a certain angle, ϑ . In what follows, such planes will be assigned by the corresponding value of ϑ . Therefore, one of the symmetry planes will be assigned as $\vartheta = 0$. It is important to realize that in this system, five more symmetry planes at torsion angles $\vartheta = \pi n/3$ [$n = 1, 5$] are encountered. All other (torsion) planes are not planes of symmetry. The torsion planes that deviate most from the symmetric planes are those assigned by the torsion angles $\vartheta = (2n + 1)\pi/6$; $n = [0, 5]$.

The main issue in the present article is to reveal the effects of the symmetric *ci* lines on the corresponding NACTs on the torsion planes. For this purpose, we compare NACTs obtained for the symmetric plane (characterized as the plane $\vartheta = 0$) with those calculated at the torsion plane characterized by $\vartheta = \pi/6$.

In the next section, we briefly describe the calculations and discuss in detail the numerical results, namely, the NACTs and the relevant topological phases. Section III presents a model that explains the numerical findings, and in the last section we discuss these findings and summarize the conclusions.

II. Numerical Treatment

Like in previous cases,^{4,6,16a} the NACTs (and the adiabatic hypersurfaces) are calculated at the state-average CASSCF level using the 6-311G** basis set.²⁶ We used the active space, including two valence electrons distributed on five orbitals (three of them belonging to the irreducible representation of A'). Three electronic states were computed with equal weights. All seven atoms were considered, but, as was mentioned earlier, the search for *ci*'s is carried out by activating only one amine hydrogen. We carried out the ab initio study by employing the MOLPRO package.²⁵

To follow the motion of the hydrogen, we use two (polar) coordinates, the radial coordinate, q , and the angular coordinate, φ , defined for a system of coordinates located at some point (R_1, θ_1) in the torsion plane. (See Figure 1.) The detection is done by calculating the angular NACT, $\tau_{\varphi 12}(\varphi, q|\vartheta, \mathbf{s})$, defined as

$$\tau_{\varphi 12}(\varphi, q|\vartheta, \mathbf{s}) = \langle \xi_1(\mathbf{s}_e|\varphi, q, \vartheta, \mathbf{s}) | \frac{\partial}{\partial \varphi} \xi_2(\mathbf{s}_e|\varphi, q, \vartheta, \mathbf{s}) \rangle \quad (1)$$

Here $\xi_i(\mathbf{s}_e|\varphi, q, \vartheta, \mathbf{s})$ ($i = 1, 2$) represents the two lowest electronic (adiabatic) Born–Oppenheimer (BO) eigenfunctions,²⁸ \mathbf{s}_e stands for the set of electronic coordinates, and \mathbf{s} presents the group of all nuclear coordinates excluding the two polar coordinates, φ and q , and the torsion angle, ϑ . Having defined the system of coordinates, the search for *ci*'s on a given torsion plane is done in the same way as that in the symmetric plane, namely, calculating angular NACTs along small circular contours of different radii. The next step is to derive the adiabatic-to-diabatic transformation (ADT) angle (mixing angle), $\gamma(\varphi, q|\vartheta)$.²⁹ (See also ref 1, chapter 3.1.)

$$\gamma(\varphi, q|\vartheta) = \int_0^\varphi d\varphi' \tau_{\varphi}(\varphi', q|\vartheta) \quad (2)$$

Here and in what follows, the variable \mathbf{s} is deleted.

TABLE 1: Results As Calculated for $q = 0.1 \text{ \AA}$

location ^a		symmetrical		$\alpha(q \vartheta = 30)$	$\bar{\alpha}(q \vartheta = 30)$
R_1	θ_1	$\alpha(q \vartheta = 0)$	$\bar{\alpha}(q \vartheta = 0)$		
1.63	80	0.019	1.537	0.085	1.262
1.73	95	0.011	1.506	0.038	1.366
1.8	110	0.015	1.517	0.011	1.455
1.83	130	0.003	1.528	0.004	1.512
1.8	140	0.004	1.528	0.003	1.521
1.73	155	0.003	1.528	0.002	1.524

^a For the meaning of these coordinates, see Figures 1 and 2.

In case of a closed contour, we get $\gamma(\varphi = 2\pi, q|\vartheta)$, namely

$$\gamma(\varphi = 2\pi, q|\vartheta) = \alpha(q|\vartheta) = \int_0^{2\pi} d\varphi' \tau_{\varphi}(\varphi', q|\vartheta) \quad (3)$$

where $\alpha(q|\vartheta)$ is identified as the corresponding topological phase.^{30–33} It is important to emphasize that for situations where the NACT is formed by two quasi-isolated states, it becomes quantized,^{32a} and, as a result, $\alpha(q|\vartheta)$ becomes a multiple integer of π or zero.^{4a,30–33}

Comment. The NACT calculations could not really be carried out on the symmetry plane itself because MOLPRO is not capable of yielding results for such a situation. To overcome this difficulty, we carried out the corresponding calculations for a series of planes as close as possible to the symmetry plane. The final results concerning the symmetry plane¹⁶ (and shown also in the present article; Figure 3 and Table 1) were, in fact, derived for one of these nearby planes and resemble, approximately, the situation on the symmetry plane.

Figure 3 presents the angular NACTs along 12 different circles as a function of φ with $q = 0.1 \text{ \AA}$. (The coordinates of the centers are specified in each panel.) Results for the symmetric case are presented in the first column, and results for the torsion case (at $\vartheta = \pi/6$) are presented in the second column. The curves in the various panels are characterized by two (spiky) peaks with opposite signs.¹⁶ (In particular, see ref 16b.) It is important to emphasize that the structure of the present NACTs differs significantly from the other two-peak (angular) NACTs, which are characterized by two positive maxima (along a closed contour).^{4,8}

It is important to emphasize that in all 12 (symmetric and torsion) cases, the center of coordinates is at the nitrogen, the polar axis is along the CN axis, and the second amine–hydrogen is located at $(R_2, \theta_2) = (1.0 \text{ \AA}, 120^\circ)$. (See Figure 1.)

As in our previous study,^{16a} the peaks of the various NACTs encountered on the symmetry plane are applied to form the so-called line of *cis* (namely, a continuous line that hosts the infinite number of *ci*'s). The same procedure is also employed to form the quasi-*ci* line on the plane $\vartheta = \pi/6$. In this stage, it is important to emphasize that because the planes do not fulfill any symmetry, the above-mentioned quasi-*ci* line is not a seam. This issue is further discussed in Sections III and IV.

In Figure 2a are presented the two lines; however, they overlap to the level that no distinction can be seen. Along these lines are marked the positions of the various centers of the circular contours mentioned earlier. Whereas in Figure 2a the two lines are presented in a somewhat arbitrary x – y plane, more information is given in Figure 2b. In this Figure, it is shown how the lines are related to other parts of the molecule. For instance, it is noticed that the first center (on the left-hand side) is closest to the methyl group and the last one is the closest to the (second) amine hydrogen.

In Table 1 are presented values of various line integrals. The results in columns 3 and 5 are the topological phases, $\alpha(q|\vartheta)$, as obtained from eq 3, and the results in columns 4 and 6 stand for the average values for the integral under each peak. (See Figure 3.) These values are approximately given by the expression

$$\bar{\alpha}(q|\vartheta) = \frac{1}{2} \int_0^{2\pi} d\varphi' |\tau_\varphi(\varphi', q|\vartheta)| \quad (4)$$

where $\bar{\alpha}(q|\vartheta)$ is defined as the intensity of the quasi-*ci*. $\bar{\alpha}(q|\vartheta)$ is a new magnitude introduced as a measure related to the quasi-seams. By definition, the topological phases due to quasi-*ci*'s are zero because the contours do not surround a *ci*. This does not mean that quasi-*ci*'s cannot affect the dynamics of the interacting nuclei. The value of $\bar{\alpha}(q|\vartheta)$ is a measure of the ability of such a quasi-*ci* to affect the dynamics. It is important to realize that $\bar{\alpha}(q|\vartheta)$ for a real *ci* is always $\pi/2$, but for the quasi-*ci*, it may attain smaller values. (The largest expected value for $\bar{\alpha}(q|\vartheta)$ is $\pi/2$.)

The results in columns 3 and 4 refer to the plane of symmetry, and those in columns 5 and 6 refer to the torsion plane. In general, the values of $\alpha(q|\vartheta)$ are ~ 0 , and the values of $\bar{\alpha}(q|\vartheta)$ are $\sim \pi/2$ with one or two exceptions for the torsion case. In this respect, we emphasize that in all previous cases (excluding the ionic systems^{34a-c}), the topological phases are (approximately) integer multiples of π (and not zero).

In a recent publication^{16b} as well as in much earlier publications,³⁴ models were introduced to explain the spiky structure of the NACTs (as given in column 1 in Figure 3). In ref 16b, we also proved that the peaks have to possess, in this situation, alternating signs (which yield $\alpha(q|\vartheta) \approx 0$). The issue of alternating signs will not be considered here.

The next section is solely devoted to the meaning of the quasi-seams on the torsion planes and in what way they differ from the ordinary seam on the symmetry plane. This study will be carried out by employing a model.

III. Model for Quasi-Seams on Torsion Planes

We start our presentation by reiterating the main difference between the symmetry plane and the corresponding *torsion* planes. Whereas the symmetry plane contains adiabatic states that may become degenerate on that plane (in other words, a degeneracy line (seam) is fully located in that plane), this cannot happen with torsion planes. Torsion planes might be characterized by accidental degeneracy points but not by a whole line. (See the discussion that follows eqs I and II.) In other words: no planar seams can be found on a torsion plane.

Because no seams are found on torsion planes, we concentrate on a different line, which is the planar intersection line between the two corresponding diabatic states. Such lines may exist on torsion planes whether or not the adiabatic states become degenerate. This line is termed, accordingly, the quasi-seam.

Now, any planar line can be defined as $p = p(S)$ where p and S are two orthogonal coordinates defined in that plane. In what follows, S is the translational coordinate defined along the line interval $[-\infty, \leq S \leq +\infty]$, and p is the corresponding orthogonal coordinate defined along a short interval (strip) in the vicinity of the quasi-seam.

Next, we consider the two diabatic potentials, $W_j(p, S|\vartheta)$ ($j = 1, 2$), and the corresponding difference, $\Delta W(p, S|\vartheta)$

$$\Delta W(p, S|\vartheta) = W_2(p, S|\vartheta) - W_1(p, S|\vartheta) \quad (5)$$

Because the quasi-seam, $p = p(S)$, is defined as the intersection line between the two diabatic potentials, its expression has to be extracted from the equation

$$\Delta W(p, S|\vartheta) = \Delta W(p(S)|\vartheta) = 0 \quad (6)$$

In general, the quasi-seam depends on ϑ ; in other words, the resulting line $p = p(S)$ may vary as a function of the torsion angle, ϑ . However, while solving eq 6, we detected, at most, a slight dependence of $p = p(S|\vartheta)$ on ϑ . This means that the various quasi-seams belonging to different torsion planes are essentially identical, a fact that allows us to assume that they all satisfy the same equation, namely, $p = p(S)$.

As mentioned earlier, we concentrate on a narrow strip that contains the $p = p(S)$ line. Within this strip, we consider the behavior of $\Delta W(p, S)$ (eq 5) and the ADT angle $\gamma(p, S|\vartheta)$ (eq 3), which can be expressed in terms of the diabatic potentials, W_1 , W_2 , and W_{12} .^{34a}

$$\gamma(p, S|\vartheta) = \frac{1}{4}\pi - \frac{1}{2} \tan^{-1} \{ \Delta W(p, S) / (2W_{12}(p, S|\vartheta)) \} \quad (7)$$

By expanding $\Delta W(p, S)$ in a Taylor series, we get the following expression (recalling that the zero-order term is zero because of eq 6)

$$\Delta W(p, S) = \frac{\partial(\Delta W(p, S))}{\partial p} \Big|_{p(S)} (p - p(S)) + O(p - p(S))^2 \quad (8)$$

To continue the treatment of $\gamma(p, S|\vartheta)$ in eq 7, we need to refer explicitly to features of W_{12} . First, we recall that because of eq II, $W_{12}(p(S), S, \vartheta) \equiv 0$ on the symmetry plane, namely, when $\vartheta = 0$. In what follows, we assume that in the vicinity of the quasi-seam, W_{12} is independent p and depends only on S (and ϑ). Combining the two features, we get

$$W_{12}(p, S|\vartheta) = \begin{cases} W_{12}(S|\vartheta); & \vartheta > 0 \\ 0; & \vartheta = 0 \end{cases} \quad (9)$$

This assumption enables us to introduce a new variable, $\kappa(S|\vartheta)$, defined as

$$\kappa(S|\vartheta) = 2W_{12}(S|\vartheta) \left[\frac{\partial(\Delta W(p, S))}{\partial p} \Big|_{p(S)} \right]^{-1} \quad (10)$$

Substituting eqs 8–10 into eq 7 yields for $\gamma(p, S|\vartheta)$ (following the neglect of the second term in eq 8)

$$\gamma(p, S|\vartheta) = \frac{1}{4}\pi - \frac{1}{2} \tan^{-1} \{ (p - p(S)) / \kappa(S|\vartheta) \} \quad (11)$$

Differentiating $\gamma(p, S|\vartheta)$ with respect to p yields, τ_p , the orthogonal component of the corresponding NACT

$$\tau_p^{(\kappa)}(p, S|\vartheta) = \frac{1}{2} \frac{\kappa(S|\vartheta)}{\kappa(S|\vartheta)^2 + \{p - p(S)\}^2} \quad (12)$$

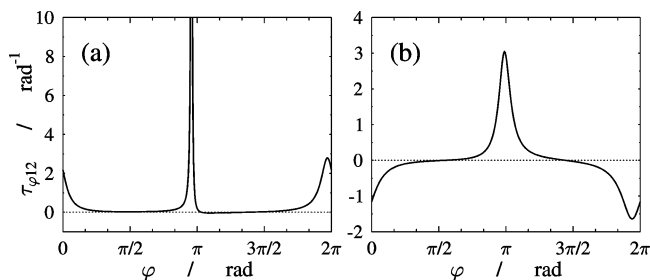


Figure 4. Angular NACTs (τ_φ) (eq 1) as a function of φ calculated along circular contours ($q = 0.1$ Å) located on the relevant tilted planes. The NACTs in part a are along a contour surrounding the ci line in the symmetry plane, and the NACTs in part b are along a contour surrounding the quasi- ci line in the torsion plane $\vartheta = \pi/6$. The corresponding phases (eq 3) are: (a) $\alpha = 2.96$ rad due to the ci line and (b) $\alpha = 0.0025$ rad due to the quasi- ci line. The centers of the two circles are located at $(R_1, \theta_1) = (1.8 \text{ Å}, 108^\circ)$, and the two planes are tilted by 10° .

Equation 12 indicates that as long as ϑ differs from zero (namely, as long as the line is located on one of the torsion planes), τ_p behaves like the Breit–Wigner function (because $\kappa(S|\vartheta)$ differs from zero). The most that happens is that it becomes spiky (in the vicinity of the quasi-seam) but never to the extreme of being singular. To find out what happens on the symmetry plane, we need to trigger a limiting process that allows ϑ to approach zero. However, recalling eqs 9 and 10 and allowing $\vartheta \rightarrow 0 \Rightarrow \kappa \rightarrow 0$, when applied to eq 12, yields the Dirac δ function at $p = p(S)$, and thus

$$\lim_{\kappa \rightarrow 0} \tau_p^{(\kappa)}(p, S) = \frac{1}{2} \pi \delta(p - p(S)) \quad (13)$$

Having the analytic expression for the orthogonal NACT in the vicinity of the (real) seam on the symmetry plane yields, along a finite value Δp of the orthogonal coordinate, p , the following value

$$\gamma(p(S)) = \frac{1}{2} \pi \int_{p(S)-\Delta p}^{p(S)+\Delta p} \delta(p - p(S)) dp = \frac{1}{2} \pi \quad (14)$$

This fact is well presented in Figure 3, where it can be seen that the NACTs on the symmetry line are consistently spikier than the corresponding NACTs located on the torsion planes.

To complete the presentation, we say that τ_p becomes singular (described by a Dirac δ function^{16,34b}) if and only if $\vartheta \rightarrow 0$, namely, when reaching the symmetry plane.

IV. Discussion and Conclusions

The main conclusion of the model study is that the ci lines on the symmetry plane possess topological effects (created by the existence of the singularities) and that the corresponding quasi- ci lines on the torsion planes do not possess this feature. The question is if there exists numerical evidence to support this conclusion?

To answer this question, we calculated angular NACTs along contours located in planes slightly tilted away (by $\sim 10^\circ$) from the above-mentioned symmetry plane and torsion plane. The contours were chosen in such a way that they surround the seam and the quasi-seam instead of intersecting them. The results are presented in Figure 4a,b, respectively. The curves in both panels clearly show a distinct form. Whereas the curve in Figure 4a is positive along the whole angular interval (typical for a contour

that surrounds a single ci or line of ci 's), the curve in Figure 4b is alternating (partially positive and partially negative) a typical curve along a contour that does not surround any ci 's (or lines of ci 's). Moreover, the corresponding line integral (eq 3) yields the value 2.96 rad, which can be considered to be π for the first case (where a ci is surrounded), and a small value (0.0025 rad) that is practically zero for the second case (where no ci is surrounded). In other words, the NACTs in the first case formed the relevant topological phase ($\alpha \approx \pi$) but failed to form it in the second case; therefore, $\alpha \approx 0$. In summary, the conclusions due to the model are in full agreement with the results of the numerical treatment on the basis of the surrounding contours in the tilted planes.

In this study is presented a phenomenon that to our knowledge so far was not discussed in the literature, namely, the existence of intra-quasi-seams associated with intraseams on a corresponding symmetry plane formed by moving a single atom in that plane. We found that although the two basic laws of quantum chemistry, as stated in eqs I and II, do not permit the existence of such intraseams on planes other than symmetry planes (for which eq II is satisfied trivially), the numerical treatment shows that intra-quasi-seams undoubtedly do exist on the corresponding torsion planes. In other words, the molecular systems found ways to surmount the quantum laws, as presented in eqs I and II, by creating intra-quasi-seams.

In this respect, two comments have to be made: (1) As is shown, quasi-seams are very similar to ordinary seams, but they may possess weaker intensities. (See eq 4 for definition.) This feature is well resembled when comparing results presented in the first three rows of Table 1. (2) Quasi-seams are characterized by the fact that $W_{12} \neq 0$, and this implies that the corresponding adiabatic potentials, $V_j(p, S|\vartheta)$ ($j = 1, 2$), do not become degenerate along $p = p(S)$. In other words, no singular NACTs (other than accidental, isolated ones) are to be found on torsion planes. This fact implies that no topological effects can be created on the torsion planes (except, eventually, because of isolated degeneracy points).

It is true that these quasi-seams are not perfect; they might be of weaker intensities and are not able to produce the Longuet–Higgins sign flip,^{2,36} but as far their relevance to dynamics is concerned, they seem to be as important as the ordinary (singular) seams.

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